CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

CANADA CENTRE FOR MINERAL AND ENERGY TECHNOLOGY

OTTAWA

MINERAL SCIENCES LABORATORIES

MRP/MSL (CF) 75-3 (P)

PROCESS FOR HIGH-TEMPERATURE ANALYTICAL SEPARATION OF VOLATILE ELEMENTS OR COMPOUNDS FROM VANADIUM PENTOXIDE MATRIX

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by

B. Nebesar

MICROMEDIA

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PROCESS FOR HIGH-TEMPERATURE ANALYTICAL SEPARATION OF VOLATILE ELEMENTS OR COMPOUNDS FROM VANADIUM PENTOXIDE MATRIX

by

B. Nebesar

FORM A (sec. 2)

REPORT OF AN INVENTION UNDER
THE PUBLIC SERVANTS INVENTIONS ACT

I. Information to be furnished by public servant inventor:

1. Name(s) of inventor(s): Boris Nebesar

2. Address(es): Residence: 33 Mason Terrace, Ottawa, Ontario. K1S 0K8

   Business: 555 Booth Street, Ottawa, Ontario. K1A 0G1

3. Nationality of inventor(s): Canadian

4. Department or Government Agency in which you are employed:

   Energy, Mines and Resources, Canada.

5. Position(s) and type of work: Research Scientist; Analytical Chemistry

6. Brief description, and drawings where necessary, of your proposal under the following headings: for (a) to (e) attached separate pages

   (a) What is the problem?

   (b) How may it be accomplished according to present knowledge?

(c) Limitations or drawbacks of present apparatus, product or process.

(d) What is your proposal?

(e) What is thought to be novel in your proposal?

7. Has any publication or disclosure to others been made? If so to whom, when and where? The existence has been mentioned several times, but no details as to appearance, dimensions, or manufacturing and the process have been divulged (1,4,5).

*8. Can you provide references in published literature of patents relating to the problem or subject? If yes, do so. Quoted in the text and at the end.

9. In your opinion does the invention belong to the Canadian Government or Crown Agency in which you are employed? Yes.

PLACE ...Ottawa, Ontario..... DATE ...December 31, 1974.....

.....Boris Belesar.....
Signature

NOTE: Where spaces are inadequate, attach separate pages.

* In addition furnish us with any communications you may have had relating to your subject.

I.6(a) An extensive study of analytical and other literature on vanadium pentoxide revealed that its practical use is limited by the lack of suitable technology which would be at the same time financially accessible to any average laboratory anywhere in the world. Vanadium pentoxide is as nearly an ideal reagent as one could wish to have for the decomposition, at high temperatures, of many substances. The subsequent analytical determinations of the more volatile components - either elements or compounds - constitute commonly the analytical field of "combustion methods". Numerous attempts to develop suitable high temperature methods, involving vanadium

pentoxide as matrix, have been hampered by its excessive reactivity with almost all commonly used materials, or by its other special properties, notably a low surface tension. A more extensive exposition of the problem and a survey of the analytically important properties of vanadium pentoxide has been given (1, 2).

(b) At present, vanadium pentoxide as matrix in the combustion methods is used predominantly in vertical high-frequency induction furnaces. A great number of methods using the resistance furnace, for the determination in particular of sulphur, exist, but vanadium pentoxide cannot easily be employed in them. Moreover, indications in the recent open literature are that the trend in the conventional determination of sulphur by the combustion method is towards the use of a porous cover, possibly in conjunction with vanadium pentoxide. These two features of my proposed improvements in the field were correctly delineated and the development started some six to eight years ago (3, 4).

(c) Limitations of the present apparatus and processes:

i) For technical reasons, vanadium pentoxide cannot be well used at high temperatures (say, 1425°C+) in the widely available standard resistance furnaces.

ii) This precludes its use as well as a matrix for standards, and a number of advantages associated with this highly successful concept.

iii) If costly high-frequency induction heating equipment cannot be purchased, as in some countries co-operating in the International Organization for Standardization (ISO), or in the developing countries, or even in any poorly endowed local institution requiring only a low sample throughput, there are few if any reliable

alternatives for the use of vanadium pentoxide.

iv) High-frequency induction heating, though amenable to the use of vanadium pentoxide as flux, must employ coupling materials which are not always desirable. This precludes an efficient application of the synthetic standards concept, described in (1, 5).

v) In a number of conventional combustion methods, not employing vanadium pentoxide, the decompositions are not as efficient as in my proposed system.

vi) Conventional methods tend recently, even without the use of vanadium pentoxide, towards the application of a combustion boat equipped with a porous filtering cover (6).

(d) Proposed is an integrated "Process for High-Temperature Analytical Separation of Volatile Elements or Compounds from Vanadium Pentoxide Matrix".

The process has several aspects:

i) A new concept for the use of vanadium pentoxide required the development of a single-use gas permeable combustion boat cover. These covers are machined from the commercially available Fiberfrax^{R} GH Board (Carborundum Co.) with conventional tools. A precisely controlled thermal conditioning at high temperatures (over 1200°C) is required to reduce blank values to acceptable levels, and to be resistant to thermal shock. In Figure 1 are shown a starting block and a machined cover.

ii) The detailed sketches of the cover are shown in Figure 2. The search for proper materials, the control methods for the chemical, mechanical, and thermal properties, together

with the gas permeability and machinability tests have already been described (7). In the following sequence of photographs we note the influence of temperature on shrinking (Figure 3), the comparison of a suitable and unsuitable material (Figure 4), the arrangement of covers on a furnace shelf prior to loading into the furnace (Figure 5), the general view of the furnace (Figure 6) and of its interior (Figure 7), and the detailed arrangement in the furnace (Figure 8). Since 1967, the complete technological cycle has been repeated nine times for the production of over 1200 boat covers of various properties. Interesting at this point is the economic aspect: the current material price is $0.12 per piece, and the machining of one boat cover takes about 30 seconds. A few additional hours are required for setting up and also for the thermal conditioning, which is performed in batches of several hundred.

iii) Although the currently manufactured product is successfully used in several applications, even better properties could be obtained in a factory with the latest technology at its disposal. This applies notably for the resistance to temperature, improvement in shrinking, in chemical blank, and the reduction of cost.

iv) The availability, in sufficient quantities, of the single use gas permeable combustion boat covers made possible an entirely new high-temperature separation process for several elements or their compounds by

using vanadium pentoxide as a versatile reagent:

a) Its phase diagrams indicate that many elements and oxides of interest in minerals and ores form homogeneous solutions at the high temperatures used. The possibility for properly controlling the behaviour of vanadium pentoxide for decompositions opened entirely new areas in research and analytical applications. The control is effected by the regulated fusion of the vanadium pentoxide. The cover affords an automatic preheat (delay) and prevents the excessive creeping of the melt, while at the same time the sample is being efficiently decomposed. A large excess of vanadium pentoxide has proved beneficial, but the process works well even down to equal amounts of vanadium pentoxide and sample.

b) Vanadium pentoxide is used as a matrix for the preparation of synthetic standards of virtually any composition down to trace levels, affording great versatility in the choice of analytical conditions.

c) Analytically useful relations between the mass of an element and a suitable readout signal have already been obtained for several elements. These relations, in the nature of calibrations, are graphically illustrated in Figure 9 for chlorine, Figure 10 for fluorine, and Figures 11 and 12 for sulphur. The correlation coefficient is for all these cases better than 0.999, indicating a nearly perfect fit.

d) This new process for high-temperature analytical separations from a vanadium pentoxide matrix has proven to be efficient, precise and accurate, and at the same time inexpensive. It should, therefore, attract the attention of the organizations, charged with the responsibility to provide analytical methods, accessible to all laboratories throughout the world, such as the International Organization for Standardization (ISO). Further it should be of interest to the laboratories of the developing nations, and, in general, to laboratories where the low sample throughput precludes the acquisition of expensive specialized instruments (8).

(e) The novelty is claimed for:

i) An improved variety of an archaic, discontinued product, still however, protected by a patent (9) and made for other purposes than that of my invention.

ii) An unusual use of an existing material, not obvious to those versed in the art of ceramic refractories.

iii) A manufacturing process for a new variety (product): the single-use gas permeable combustion boat cover.

iv) A new process for the successful analytical control of the vanadium pentoxide for high-temperature separations of a number of elements. These now include chlorine, fluorine, and sulphur, but should be applicable, by extension of the same principles, to all elements or compounds, volatile at the operational temperatures.

v) This integrated process has enabled me to attain increased efficiency in the hitherto unsolved problems of calibration and determination of sulphur in some materials (10, 11).

vi) The process reduces, by its efficiency and versatility, the cost of the operation, and avoids the need for the purchase of more expensive instrumentation.

REFERENCES

1. B. Nebesar, "Vanadium Pentoxide as a Versatile, High-Temperature Separation Reagent", Paper No. 178 (Abstract), Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1974, Cleveland, Ohio.

2. B. Nebesar, "Vanadium Pentoxide as a Versatile, High-Temperature Separation Reagent", Paper No. 178, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1974, Cleveland, Ohio.

3. B. Nebesar, "Critical Review of the Hot-Zone Dust-Filtering Devices Used in the Combustion Method for Sulphur Determination", Laboratory Practice 18, 1290 (1969).

4. B. Nebesar, "Technique for Mounting and Measuring Gas Permeability of Soft, Sheet-Form Refractories", Material Research and Standards 10, 76 (1970).

5. B. Nebesar, "Optimization of the Combustion Method for the Determination of Sulphur Using a Resistance Furnace", Paper No. 30, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1972, Cleveland, Ohio.

6. D. J. Charette, "Report on the Seventh Meeting of ISO/TC 102/SC 2, Held in Ottawa, Ontario, May 27, 1974 to May 30, 1974 inclusive", MS-SM 74-27, Standards Memorandum, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, October 9, 1974, p. 20.

7. B. Nebesar, "New Single-Use Boat Covers for Dust Control in Combustion Sulphur Analysis", MS-PP 68-52, Division Report, Mineral Sciences Division, Mines Branch,

Department of Energy, Mines and Resources, January 23, 1969, unpublished.

8. B. Nebesar, "Specialized Instruments for the Determination of Sulfur by the Combustion Method", Journal of Chemical Education 48, A 751 (1971); 49, A 9 (1972); 49, A 63 (1972).

9. G.J. Krasl, "Gas Analysis for Sulphur" Canadian Patent 560, 386; July 15, 1958.

10. B. Nebesar, "Semi-Automatic Gravimetric Spectrophotometric Titration System with a Digital Readout", Paper No. 51, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1973, Cleveland, Ohio.

11. B. Nebesar, "Limit of Detection in the Determination of Sulphur by the Combustion Method Using the Visual and Spectrophotometric Iodometry", to be submitted to the Journal of Testing and Evaluation.

II. **Remarks of Divisional Head:**

1. Did the invention arise from a general programme of research or from work in relation to a particular piece of equipment, process or problem?

2. Development contract existing or projected, if any.

3. Other persons or organizations participating.

4. Has the apparatus, product or process been made or tested?

5. What are the possible commercial applications of the invention and their extent?

6. What are the actual or potential uses of the invention by the armed forces or other government agencies?

7. Comments, if any, on inventor's answers.

8. Other remarks.

PLACE ..... DATE .....

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Signature

NOTE: Where spaces are inedaquate, attach separate pages.

CPDL 1033
June 1968

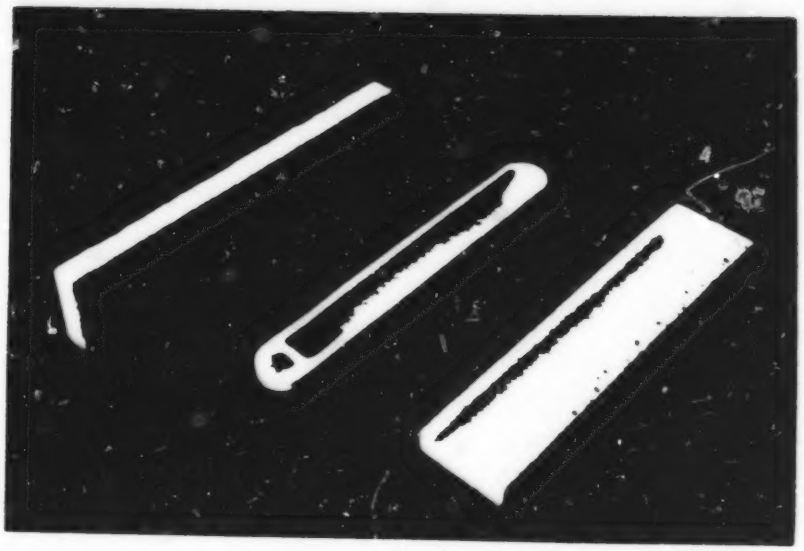
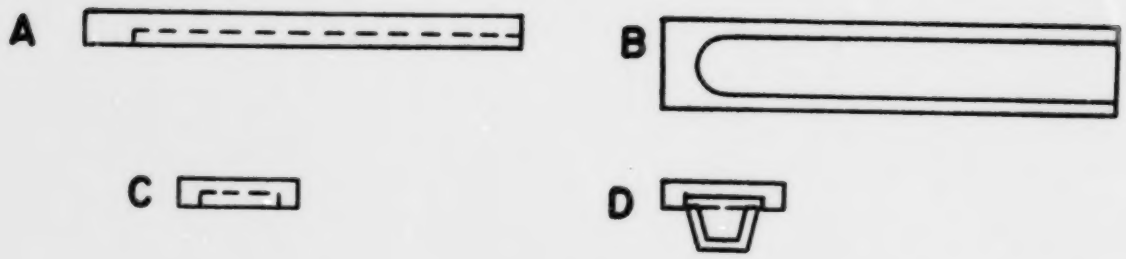


Figure 1. Block of the original material, boat, and the machined cover.

GAS-PERMEABLE COMBUSTION BOAT COVERS



A Elevation, sideways

B Plan, bottom

C Elevation, end, front

D Elevation, end, back, with boat

Figure 2.

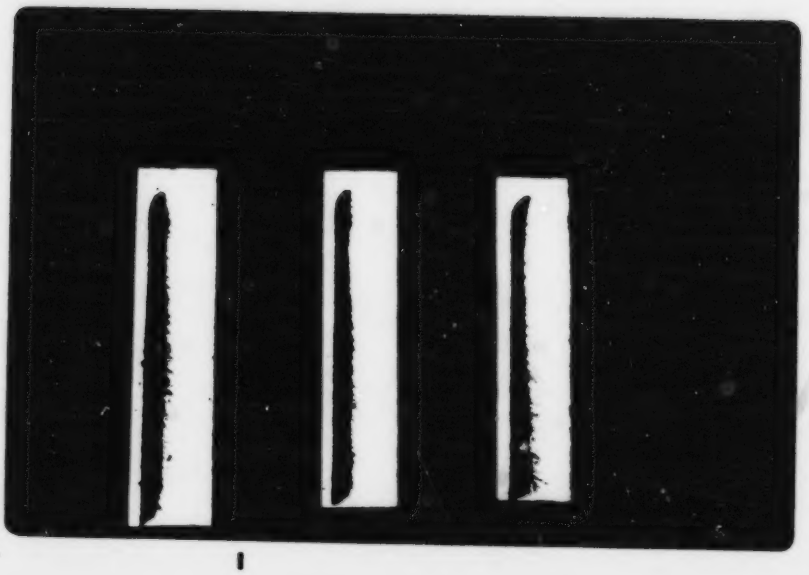


Figure 3. Influence of temperature on shrinking of covers.

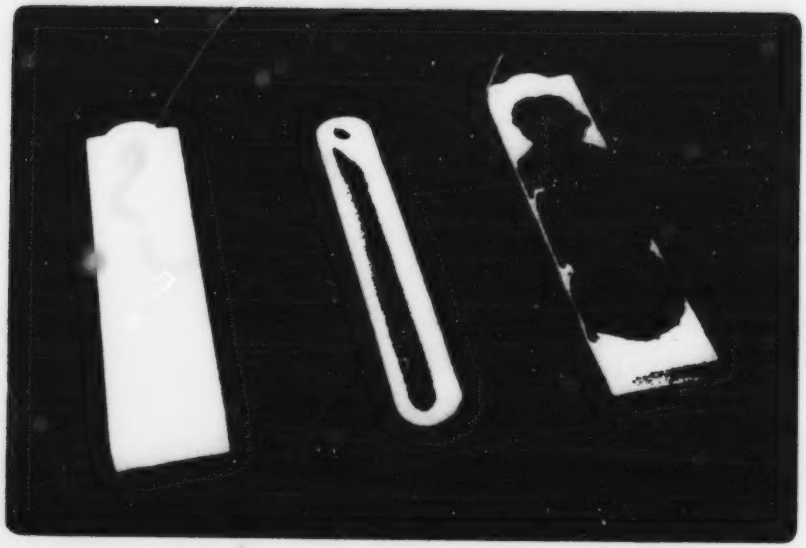


Figure 4. Comparison of a suitable and unsuitable cover material.

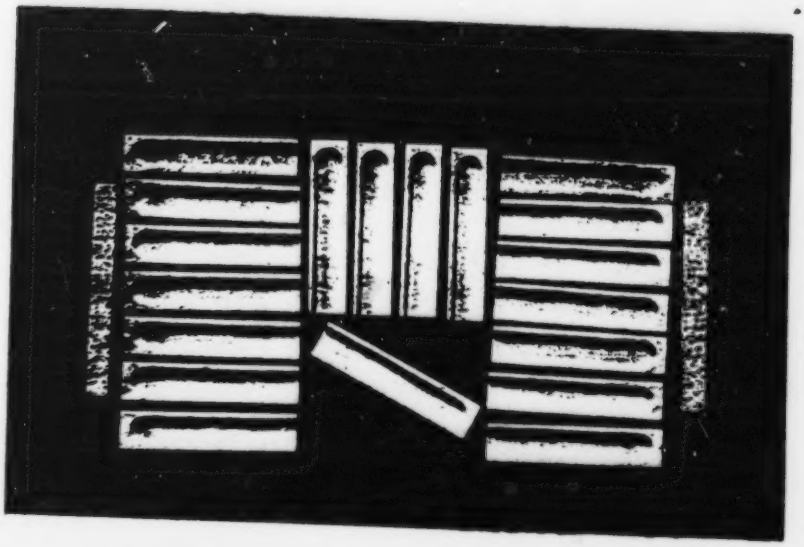


Figure 5. Arrangement of covers on a furnace shelf.

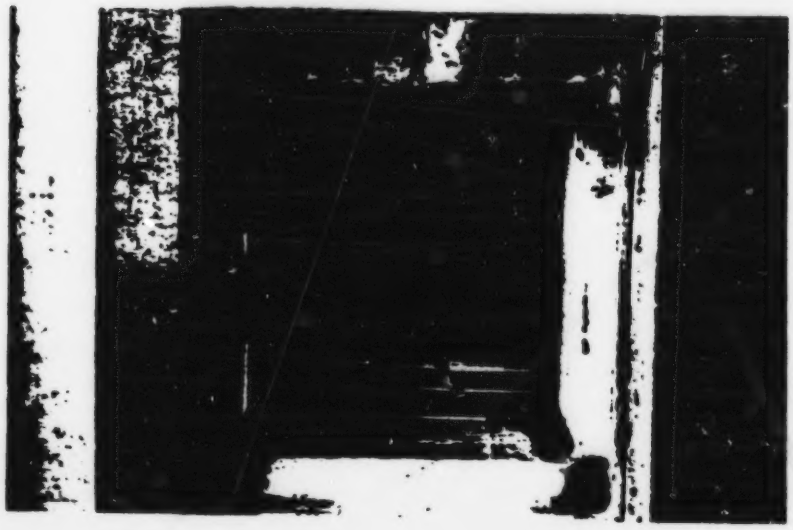


Figure 6. General view of the furnace.

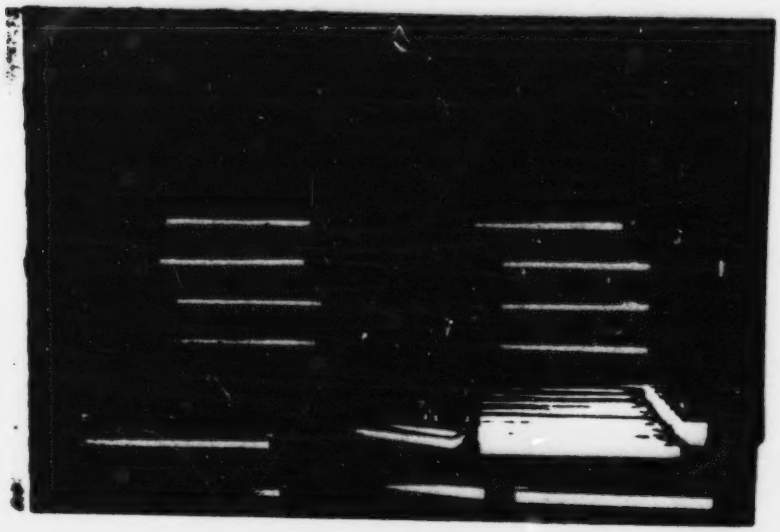


Figure 7. Interior of the furnace.

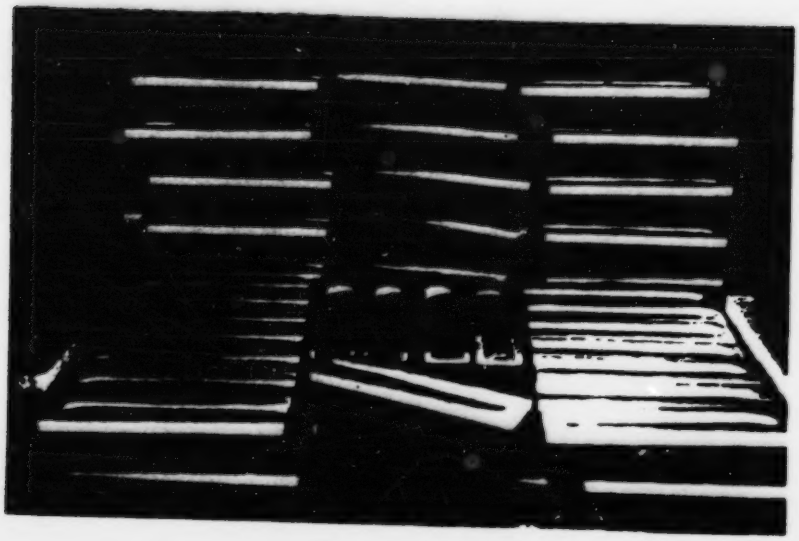


Figure 8. Detailed arrangement in the furnace.